(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 875 546 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.11.1998 Bulletin 1998/45

(51) Int Cl.[6]: **C09D 167/06**, C09D 133/06

(21) Application number: **98303284.8**

(22) Date of filing: **28.04.1998**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **01.05.1997 US 847115**

(71) Applicant: **FIBRE GLASS-EVERCOAT COMPANY, INC.**
Cincinnati, OH 45242 (US)

(72) Inventors:
- **Parish, David Michael**
  Loveland, Ohio 45140 (US)
- **Fron, William Ronald**
  Milford, Ohio 45150 (US)

(74) Representative: **Perry, Robert Edward**
GILL JENNINGS & EVERY
Broadgate House
7 Eldon Street
London EC2M 7LH (GB)

(54) Sprayable acrylate-based coating composition

(57) A sprayable coating composition comprises a resin system comprising 30 to 96 wt. % of a resin component, 1 to 30 wt. % of a multifunctional acrylate component, and 1 to 15 wt. % of a monofunctional acrylate component; and a catalyst component. The resin system is blended with the catalyst component, either internally or externally of a spray nozzle, and the resultant sprayable coating composition is sprayed onto a substrate. The resulting cured coating provides a surface which is water-resistant and mar-resistant, and has generally improved physical properties.

EP 0 875 546 A2

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

The present invention relates to a sprayable coating composition, and, more particularly, to a sprayable coating composition which has improved water and mar resistance, and generally improved performance, and a method for using such a composition.

Background of the Invention

Multi-component coating compositions are widely used in the plastics and marine industries. In these compositions, a liquid resin system and a catalyst for the resin system are mixed together and are sprayed onto a substrate such that the catalyst and the resin system react and harden on the substrate. The mixing may be done immediately before spraying (referred to as an internal mixing system) or immediately after spraying (referred to as an external mixing system). For example, US-A-4967956 discloses a "gel coat" spraying system which uses a resin such as an epoxy resin or a polyester resin, a catalyst for the resin, and spraying means which includes an airless liquid nozzle. Such a gel coat utilizes a slow curing process.

Conventional coating compositions on articles often produce grey marks when the coating is scratched or contacted with a blunt instrument. When these marks form, the article is referred to as being "marred." Although it is not known for certain how the grey mar marks are produced, one possible explanation is that the mar is produced as a result of the coating being too soft to resist damage to its chemical structure. Another possible explanation is that when the coating is scratched, the bonds between the molecules which make up the coating are broken and produce the grey mar.

Additionally, conventional coatings can become damaged by the penetration of water and other chemicals into the chemical structure of the coating. These coatings allow water penetration because of open spaces in the polymeric structure of the coating which are produced during the polymerization reaction which forms the coating. Water penetrates into these openings and then expands when it freezes. The expansion of the water then causes the coating to crack and pit.

Accordingly, a need in the art still exists for a sprayable coating composition which may be easily applied to a variety of substrates, cures quickly, and has improved water and mar resistance.

Summary of the Invention

The present invention is directed to a coating composition which comprises a resin system which comprises 30 to 96 wt. % of a resin component, 1 to 30 wt. % of a multifunctional acrylate component, and 1 to 15 wt. % of a multifunctional acrylate component; and a catalyst component. Desirably, the resin component comprises an unsaturated high molecular weight polymer resin and a reactive diluent.

The novel composition is sprayable, cures quickly at ambient temperature, has improved water and mar resistance, is inexpensive to produce and can be formulated to be styrene-free. The coating composition of this invention also provides generally improved physical properties. The composition may be used on a mould surface during a moulding process as a "gel coat" or as a surface coating on the surface of an article. When used on an exterior surface of an article, the coated article can be provided with a smooth and glossy appearance, which is weatherable due to the water-resistant character of the coating. Additionally, because the coating composition of the present invention cures at room temperature, it requires no external heat source to cure.

The resin system may also include (with amounts given by way of example) up to 2.0 wt. % of a thixotropic agent; up to 0.5 wt. % of an activating agent; up to 30 wt. % of a pigment; up to 30 wt. % of a pigment extender; up to 1.0 wt. % of an anti-settling additive; up to 1.0 wt. % of an anti-foaming additive; up to 0.5 wt. % of an accelerating agent; up to 1.0 wt. % of an UV stabilizer; up to 0.75 wt. % of a promoter; and up to 2.0 wt. % of a co-promoter.

In a preferred embodiment, the multifunctional acrylate component is selected from difunctional acrylates, difunctional methacrylates and mixtures thereof. In a more preferred embodiment, the multifunctional acrylate component additionally comprises a trifunctional acrylate component selected from trifunctional acrylates, trifunctional methacrylates and mixtures thereof. In a particularly preferred embodiment, the multifunctional acrylate component is a mixture comprising 1 wt. % to 15 wt. % of the difunctional acrylate component and from 1 wt. % to 15 wt. % of the trifunctional acrylate component.

The invention also includes a method for using a coating composition, comprising forming the resin system, adding a catalyst component to the resin system to form a sprayable coating composition; and spraying the coating composition onto a substrate.

Description of the Invention

One aspect of the present invention is directed to a sprayable coating composition comprising a resin system and a catalyst component. The resin system comprises a resin component, a multifunctional acrylate component, and a monofunctional acrylate component. The resin component will be discussed first.

The resin component comprises a resin and a reactive diluent. Typically, resin components are supplied by the manufacturer in this form. Desirably, the resin is an unsaturated high molecular weight polymeric resin. Useful resins are selected from isophthalic esters, vinyl

esters, vinyl polyesters, bisphenols, unsaturated acrylic resins, and mixtures thereof. Desirably, the resin component is styrene-free, i.e., free of a styrene monomer reactive diluent. The preferred resin component is DION V-7000, which is a proprietary mixture of an unsaturated isophthalic polyester resin and a vinyl toluene reactive diluent and which is provided from the manufacturer free of a styrene carrier. This resin component is available from Reichhold Chemicals, Inc. of Research Triangle Park, Durham, North Carolina, USA.

The reactive diluent is provided to adjust the viscosity of the resin to maintain the resin component in a liquid state for spraying and also participates in the polymerization reaction. Useful reactive diluents include vinylbenzene (styrene), vinyltoluene and mixtures thereof. Vinyltoluene is preferred; it is safer to use than vinylbenzene because vinyltoluene has a lower vapour pressure, a higher boiling point and a higher flash point than styrene. Additionally, when vinyltoluene is used, fume hoods or special application equipment are unnecessary.

The present invention employs a combination of a multifunctional acrylate component and a monofunctional acrylate component. As used in this specification, the prefix "multi" means "having more than one", and is not restricted to two or more. For the purpose of this specification, the term "acrylate component" shall be construed to include acrylates, methacrylates and mixtures thereof. A "monofunctional" acrylate is one having an average functionality of one or less.

In this invention, a multifunctional acrylate component in combination with a monofunctional acrylate component is employed to increase the crosslink density of the coating. The use of a multifunctional acrylate component in combination with a monofunctional acrylate component produces an interpenetrating network of chemical bonding having an increased amount of crosslinking. This interpenetrating network produces a surface coating which inhibits the penetration of water and other chemicals.

The coating composition is also highly resistant to marring and fading. Because of the high degree of crosslinking, the coating is particularly resistant to marring. When the surface of an article, which has been coated with the coating composition of this invention, is scratched, no grey marks are formed. Additionally, unlike aromatic acrylics, aliphatic acrylates and methacrylates have a natural resistance to ultraviolet radiation because they do not contain aromatic groups which are generally susceptible to yellowing when subjected to UV radiation. Because it employs aliphatic acrylates and methacrylates, the coating composition of this invention is also resistant to fading.

In addition to providing mar, UV and water resistance, the acrylates and methacrylates employed in the coating composition of this invention also serve as reactive diluents. In other words, the acrylates participate in the reaction with the resin and do not evaporate, exude or plasticize as many nonreactive diluents do.

Useful monofunctional acrylates and methacrylates include allyl methacrylate, caprolactone methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, ethoxylated nonyl phenol acrylate, glycidyl methacrylate, isobornyl acrylate, isobornyl methacrylate, isodecyl acrylate, isodecyl methacrylate, isoctyl acrylate, lauryl acrylate, lauryl methacrylate, 2-phenoxy acrylate, 2-phenoxy methacrylate, polypropylene glycol monomethacrylate, stearyl acrylate, stearyl methacrylate, tetrahydrofurfuryl acrylate, tetrahydrofurfuryl methacrylate, tridecyl acrylate, tridecyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (HEMA) and mixtures thereof.

Useful difunctional acrylates and methacrylates include alkoxylated aliphatic diacrylate, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,6-hexanediol diacrylate (HDODA), 1,6-hexanediol dimethacrylate, neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, propoxylated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate and mixtures thereof.

Useful trifunctional acrylates and methacrylates include propoxylated glyceryl triacrylate, ethoxylated trimethylol propane triacrylate, pentaerythritol triacrylate, propoxylated glyceryl triacrylate, propoxylated timethylpropane triacrylate, trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tris(2-hydroxyethyl) isocyanurate trimethacrylate and mixtures thereof.

Most desirably, the coating composition of the present invention employs a HEMA as the monofunctional acrylate component, HDODA as the difunctional acrylate component and TMPTA as the trifunctional acrylate component. HDODA and TMPTA are available from Sartomer of Exton, Pennsylvania, USA, under the product designations SR 238 and SR 351, respectively. HEMA is available from Rohm & Haas of Rosemont, Illinois, USA.

The coating composition of the present invention includes a catalyst component to form a sprayable coating composition which can be sprayed onto a substrate. As used herein, the term "catalyst" refers to an organic free radical initiator. Useful catalysts include methyl ethyl ketone peroxide, benzoyl peroxide, boron trifluoride, polyamine, mercaptan, isobiurane, isocyanurate and mixtures thereof, preferably methyl ethyl ketone peroxide, benzoyl peroxide or mixtures thereof. The catalyst component is preferably present in the coating composition in an amount of 0.5 to 10 wt. %, more preferably 0.5 to 5 wt. %, of the total composition.

To increase the rate of catalysis of the polymerization reaction, the composition may include a promoter. The promoter, which is a weak catalyst itself, increases

the action of the catalyst which, in turn, increases the rate of polymerization. Useful promoters include cobalt salts, potassium salts and vanadium salts of organic acids. Desirably, the promoter is cobalt naphthenate, cobalt neodecanate, potassium 2-ethylhexanoate, vanadium 2-ethylhexanoate or a mixture thereof. A useful cobalt neodecanoate is available from Mooney Chemicals, Inc. of Cleveland, Ohio, USA, under the trade name 21% Cobalt Hydroxy Ten-Cem. A useful potassium 2-ethylhexanoate is available from Mooney under the trade name Potassium Hex-Cem 977 and a useful vanadium 2-ethylhexanoate is also available from Mooney under the trade name Cur-R_x.

To further increase the rate of catalysis of the polymerization reaction, the coating composition of the present invention may also include a co-promoter. Useful co-promoters include metal salts of organic acids, such as, for example, potassium salts, vanadium salts, calcium salts and sodium salts of organic acids. In addition to being useful as co-promoters, potassium salts of organic acids also prevent the coating from yellowing as it cures and also help the coating retain its colour over time. Desirably, the co-promoter will be potassium carboxylate which is available from Westbridge Industries of Plainfield, New Jersey, USA, under the trade name Westdry P Promoter.

To decrease curing time, the resin system may also include an accelerating agent. The coating composition of this invention typically thickens to a suitable coating in about 20 minutes. In certain situations, it is desirable to decrease the curing time of the coating. By including an accelerating agent in the composition of this invention, the curing time of the coating composition can be reduced to, say, 2.5-3 minutes. One skilled in the art will realize that the choice to use an accelerating agent is application-specific and thus an accelerating agent is not always necessary. Suitable accelerating agents are substituted aromatic amines and mixtures thereof. Useful accelerating agents include N,N'-dimethyl-p-toluidine (DMPT), dimethylaniline (DMA) and diethylaniline (DEA). Desirably, the accelerating agent is DMPT which is available from First Chemical Corporation of Pascagoula, Mississippi, USA.

To produce a coloured coating, the resin system may also include a pigment, e.g. an inorganic pigment, organic pigment or mixture thereof. Exemplary inorganic pigments include black iron oxide, available from Pfizer, and titanium dioxide, TiO_2 (rutile), available from SCM Chemicals under the designation Tiona RCL-9. Another useful pigment is lithopone which is a white pigment comprising zinc sulfide, barium sulfate and zinc oxide. Lithopone is available from Sino-American Pigment Systems, Inc., of Emeryville, California, USA. Exemplary organic pigments include phthalocyanine blues and greens.

Because of the high costs of some pigments, the composition of the present invention may also include pigment extenders, when pigments are used. Extenders replace a portion of the pigment to reduce the amount of pigment used in the composition and to consequently reduce the cost of the pigment. Useful extenders include lithopone, alumina trihydrate, calcium carbonate and mixtures thereof.

The resin system may optionally include a thixotropic agent. Useful thixotropic agents include hydrophilic fumed silica, hydrophobic fumed silica and organic clays. Desirably, the composition of this invention will include a hydrophilic fumed silica. If a fumed silica is used, desirably it will have a BET surface area of 200 m^2/g. A useful hydrophilic fumed silica is commercially available from DeGussa Co. of Ridgefield Park, New Jersey, USA, under the trade name Aerosil 200.

To activate the fumed silica, the invention may include an activating agent. Useful activating agents are polyethers and polyalcohols. The preferred activating agent is ethylene glycol.

To prevent pigments and fillers from settling out of solution, the resin system may also include an anti-settling additive. The anti-settling additive both reduces settling and facilitates the redispersion of the pigments and fillers if they settle out. By using an anti-settling additive, the shelf-life of the composition can be increased. A useful anti-settling additive is BYK®-W 966 which is a solution of polyamine amides and acidic polyesters. The formulation of this additive is proprietary to and produced by Byk-Chemie USA of Wallingford, Connecticut, USA. Alternatively, fumed silicas or organoclays can be added to the composition to increase its thixotropy which, in turn, helps to maintain the pigments and other fillers in solution.

As the coating composition is applied to an article, air bubbles can form on the surface of the coating. As the coating cures, these air bubbles either can become entrapped in the coating or can break, causing the article to have a roughened, pitted surface. To prevent air bubbles from forming, the composition can include an air release agent which reduces the amount of foam generated during the application process. In turn, when an air release agent is used, the quality of the coating surface is improved. A useful air release agent is BYK A 555, which is a proprietary air release agent produced by Byk-Chemie USA. Other useful air release agents are available from Estron Chemical, Inc. of Calvert City, Kansas, USA, under the trade names Resiflow LF, Resiflow L, Resiflow LV, Resiflow LX, Resiflow L-67, Resiflow LV-67, Resiflow L-237, Resiflow LH-240 and Resiflow LG99.

If the coating composition of the present invention is intended to be used on articles which will be exposed to ultraviolet radiation, e.g. articles which will be exposed to sun light, the resin system may also include an UV stabilizer. UV stabilizers absorb UV radiation, preventing the radiation from affecting the polymer portion of the coating. One skilled in the art will appreciate that an UV stabilizer is unnecessary if the coating composition is not used in an application where it will be exposed

to UV radiation. Useful UV stabilizers include substituted silicon oligomers, substituted benzotriazoles and mixtures thereof. A suitable a substituted silicon oligomer is polymethylpropyl-3-oxy[4-(2,2,6,6-tetramethyl)piperidinyl]-siloxane which is available from Great Lakes Chemical Corp. of West Lafayette, Indiana, USA, under the trade name Uvasil 299 HM. Another useful UV stabilizer is 2-(2'-hydroxy-5'-methylphenyl)benzotriazole which is available from Great Lakes Chemical under the trade name Lowilite 55. Still another useful UV stabilizer is 2-(2-hydroxy-5-t-octylphenyl)benzotriazole available from American Cyanamid Company of Wayne, New Jersey, USA, under the product name Cyasorb® UV 5411. Still another useful UV stabilizer is Tinuvin 123, which is decanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidinyl) ester, reaction products with 1,1-dimethylethylhydroperoxide and octane. Tinuvin 123 is available from Ciba Additives of Tarrytown, NJ, USA.

The coating composition of the present invention preferably comprises a resin system which comprises 40 to 70 wt. % of a resin component, 1 to 20 wt. % of a multifunctional acrylate component, and 1 to 12 wt. % of a monofunctional acrylate component; and a catalyst component. The resin system may optionally include up to 1.5 wt. % of a thixotropic agent; up to 0.3 wt. % of an activating agent; up to 20 wt. % of a pigment; up to 20 wt. % of a pigment extender; up to 0.75 wt. % of an anti-settling additive; up to 0.75 wt. % of an anti-foaming additive; up to 0.25 wt. % of an accelerating agent; up to 0.75 wt. % of an UV stabilizer; up to 0.5 wt. % of a promoter; and up to 1.5 wt. % of a co-promoter. The multifunctional acrylate component preferably comprises 1 to 10 wt. % of each of difunctional and trifunctional acrylate components.

Most preferably, the coating composition of the present invention comprises a resin system which comprises 50 to 60 wt. % of an unsaturated resin component, 1 to 10 wt. % of a multifunctional acrylate component, and 1 to 10 wt. % of a monofunctional acrylate component; and a catalyst component. The resin system may optionally include up to 1.0 wt. % of a thixotropic agent; up to 0.25 wt. of an activating agent; up to 10 wt. % of a pigment; up to 10 wt. % of a pigment extender; up to 0.5 wt. % of an anti-settling additive; up to 0.5 wt. % of an anti-foaming additive; up to 0.10 wt. % of an accelerating agent; up to 0.5 wt. % of an UV stabilizer; up to 0.3 wt. % of a promoter; and up to 1.0 wt. % of a co-promoter. Most preferably, the multifunctional acrylate component comprises 1 to 5 wt. % of each of difunctional and trifunctional acrylate components.

In the method of the present invention, the catalyst component can be added to the resin system during the spraying step either externally or internally of the spray nozzle. For example, the catalyst component can be sprayed with the resin system and blended externally using a dual spray gun such as, for example, the PRED/FRP equipment available from Binks of Franklin Park, Illinois, USA. The catalyst component may also be mixed with the resin system internally of the spray coat system before spraying. One skilled in the art will appreciate that if the resin system includes an accelerator, the coating composition must be sprayed immediately after the resin system and catalyst are mixed, to avoid clogging of the spray nozzle caused by the curing of the coating composition.

The coating composition of the present invention cures at room temperature. Because it cures at room temperature, expensive heat curing equipment, such as an external heat source or oven, is unnecessary. Further, the quick curing time makes the coating composition of this invention convenient to use. Finally, because it can be formulated to be free of a vinylbenzene monomer, it is unnecessary to use a fume hood during its application.

The following formulation illustrates the invention (amounts given in parts by wt):

Dion V-7000	55
Potassium hex	0.4
Cyasorb UV 5411	0.3
BYK A 555	0.15
BYK w-966	0.2
TiO_2	2.5
Lithopone	2.5
Aerosil 200	0.75
Camel Wite	7.5
Multifex MM	5
Ethylene Glycol	0.5
Cobalt	0.2
DMPT	0.02
HDODA	2
TMPTA	2
HEMA	7

Claims

1. A sprayable coating composition comprising a resin system comprising 30 to 96 wt. % of a resin component, 1 to 30 wt. % of a multifunctional acrylate component, and 1 to 15 wt. % of a monofunctional acrylate component; and a catalyst component.

2. The composition of claim 1, wherein the resin component includes a resin and a reactive diluent.

3. The composition of claim 1 or claim 2, wherein the resin component is styrene-free.

4. The composition of any preceding claim, wherein the resin is selected from isophthalic esters, vinyl esters, vinyl polyesters, bisphenols, unsaturated acrylic resins, and mixtures thereof.

5. The composition of any preceding claim, wherein the multifunctional acrylate component is selected from difunctional acrylates, difunctional methacrylates and mixtures thereof.

6. The composition of claim 5, wherein the multifunctional acrylate component is a mixture comprising 1 to 15 wt. % of a difunctional acrylate component selected from difunctional acrylates, difunctional methacrylates and mixtures thereof, and 1 to 15 wt. % of a trifunctional acrylate component selected from trifunctional acrylates, trifunctional methacrylates and mixtures thereof.

7. The composition of any preceding claim, further including up to 0.75 wt. % of a polymerization promoter, e.g. a cobalt salt of an organic acid.

8. The composition of claim 7, further including up to 2 wt. % of a co-promoter, e.g. a potassium salt of an organic acid.

9. The composition of any preceding claim, further including up to 1.0 wt. % of an air-release agent selected from foam-destroying polymers, polydimethylsiloxanes and mixtures thereof.

10. The composition of any preceding claim, further including up to 1 wt. % of an anti-settling additive selected from polyamine amides and acidic polyesters, organoclays and mixtures thereof.

11. The composition of any preceding claim, further including up to 30 wt. % of a pigment.

12. The composition of claim 11, further including up to 30 wt. % of a pigment extender selected from alumina trihydrate, calcium carbonate, lithopone and mixtures thereof.

13. The composition of any preceding claim, further including up to 2 wt. % of a thixotropic agent selected from hydrophilic fumed silica, hydrophobic fumed silica and organoclay compounds, and optionally also including up to 0.5 wt. % of a synergist for the thixotropic agent.

14. The composition of any preceding claim, further including up to 1 wt. % of a UV stabilizer.

15. The composition of any preceding claim, further including up to 0.5 wt. % of an accelerating agent.

16. The composition of any preceding claim, wherein the resin system comprises 40 to 70 wt. % of the resin component, 1 to 20 wt. % of the multifunctional acrylate component, and 1 to 12 wt. % of the monofunctional acrylate component.

17. The composition of claim 16, further comprising up to 1.5 wt. % of a thixotropic agent; up to 0.3 wt. % of an activating agent; up to 20 wt. % of a pigment; up to 20 wt. % of a pigment extender; up to 0.75 wt. % of an anti-settling additive; up to 0.75 wt. % of an anti-foaming additive; up to 0.25 wt. % of an accelerating agent; up to 0.75 wt. % of an UV stabilizer; up to 0.5 wt. % of a promoter; and up to 1.5 wt. % of a co-promoter.

18. The composition of claim 16, wherein the resin system comprises 50 to 60 wt. % of the resin component, 1 to 10 wt. % of a multifunctional acrylate component, and 1 to 10 wt. % of the monofunctional acrylate component.

19. The composition of claim 18, further comprising up to 1 wt. % of a thixotropic agent; up to 0.25 wt. % of an activating agent; up to 10 wt. % of a pigment; up to 10 wt. % of a pigment extender; up to 0.5 wt. % of an anti-settling additive; up to 0.5 wt. % of an anti-foaming additive; up to 0.10 wt. % of an accelerating agent; up to 0.5 wt. % of an UV stabilizer; up to 0.3 wt. % of a promoter; and up to 1 wt. % of a co-promoter.

20. A method for coating a substrate, which comprises adding a catalyst component to a resin system, to form a sprayable coating composition as defined in any preceding claim; and spraying the coating composition onto the substrate.